

**PATENT APPLICATION
IN THE
UNITED STATES PATENT AND TRADEMARK OFFICE**

TITLE: PRIMARY INTERMEDIATES FOR OXIDATIVE COLORATION OF HAIR

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PRIMARY INTERMEDIATES FOR OXIDATIVE COLORATION OF HAIR

Field of the Invention

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This invention relates to new benzene-1,4-diamine compounds and compositions containing these compounds as primary intermediates for oxidative coloring of hair fibers.

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Background to the Invention

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Coloration of hair is a procedure practiced from antiquity employing a variety of means. In modern times, the method most extensively to color hair is an oxidative dyeing process utilizing one or more oxidative hair coloring agents in combination with one or more oxidizing agents.

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Most commonly a peroxy oxidizing agent is used in combination with one or more oxidative hair coloring agents, generally small molecules capable of diffusing into hair and comprising one or more primary intermediates and one or more couplers. In this procedure, a peroxide material, such as hydrogen peroxide, is employed to activate the small molecules of primary intermediates so that they react with couplers to form larger sized compounds in the hair shaft to color the hair in a variety of shades and colors.

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A wide variety of primary intermediates and couplers have been employed in such oxidative hair coloring systems and compositions. Among the primary intermediates employed there may be mentioned p-phenylenediamine, p-toluenediamine, p-aminophenol, 4-amino-3-methylphenol, N,N-bis(2-hydroxyethyl)-p-phenylene diamine, 1-(2-hydroxyethyl)-4,5-diaminopyrazole and as couplers there may be mentioned

resorcinol, 2-methylresorcinol, 3-aminophenol, 2,4-diaminophenoxyethanol, and 5-amino-2-methylphenol.

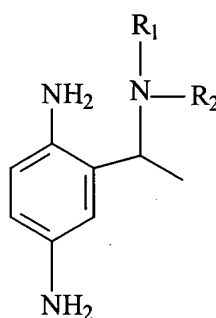
There are numerous additional requirements for oxidation dye compounds that are used to dye human hair besides the color or the desired intensity. Thus, the dye compounds must be unobjectionable in regard to toxicological and dermatological properties and must provide the desired hair color with a good light fastness, fastness to a permanent wave treatment, acid fastness and fastness to rubbing. The color of the hair dyed with the dye compounds in each case must be stable for at least 4 to 6 weeks to light, rubbing and chemical agents. Furthermore, an additional requirement is the production of a broad palette of different color shades using different developer and coupler substances. A majority of the desired shades have been produced with dyes based on p-phenylene-diamine. However, use of p-phenylenediamine is being questioned, mainly due to a sensitization potential. GB 2,239,265A describes that some individuals are becoming sensitized to p-phenylenediamine and its derivatives. The proposed replacements for p-phenylenediamine have not proved entirely satisfactory. There is therefore a need for new primary intermediate compounds to meet one or more of the desired properties but not possessing the sensitization potential possessed by p-phenylenediamine, that is, which has a significantly weaker sensitization potential than p-phenylenediamine.

Summary of the Invention

It is therefore an object of this invention to provide new primary intermediate compounds useful in place of p-phenylenediamine to provide a wide range of different color shades with various combinations of primary intermediates and couplers, but which has a weaker sensitization potential than p-phenylenediamine.

It has been discovered that new benzene-1,4-diamine derivative compounds are suitable primary intermediates for hair coloring compositions and systems for providing good oxidative coloration of hair and for providing acceptable light fastness, good selectivity, fastness to shampooing, fastness to perspiration and permanent wave treatment, and suitable for providing a wide variety of different color shades with various primary intermediate and coupler compounds.

The invention provides new benzene-1,4-diamine compounds of Formula (1):



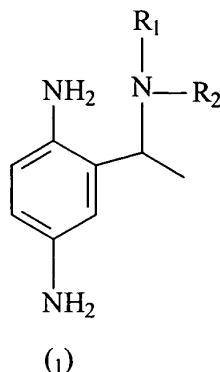
(1)

wherein R_1 and R_2 are each individually selected from hydrogen atoms, C_1 to C_5 alkyl, C_1 to C_5 mono or dihydroxyalkyl, phenyl or benzyl optionally substituted with a hydroxyl, amino or C_1 to C_3 alkoxy group, or R_1 and R_2 together with the nitrogen atom to which they are attached form a C_3 to C_6 , preferably C_4 to C_6 , saturated or unsaturated ring optionally containing in the ring one or more additional hetero atoms selected from O, S and N atoms.

These novel primary intermediates are used to provide coloration to hair in which there is good dye uptake by the hair and provides shades or colors which are stable over a relatively long period of time. The novel primary intermediates provide for dyeing of hair that provides color or shades that possess good wash fastness and do not undergo the significant changes on exposure to light or shampooing.

Detailed Description of the Invention

Preferred benzene-1,4-diamine derivative compounds of this invention are those of formula (1)

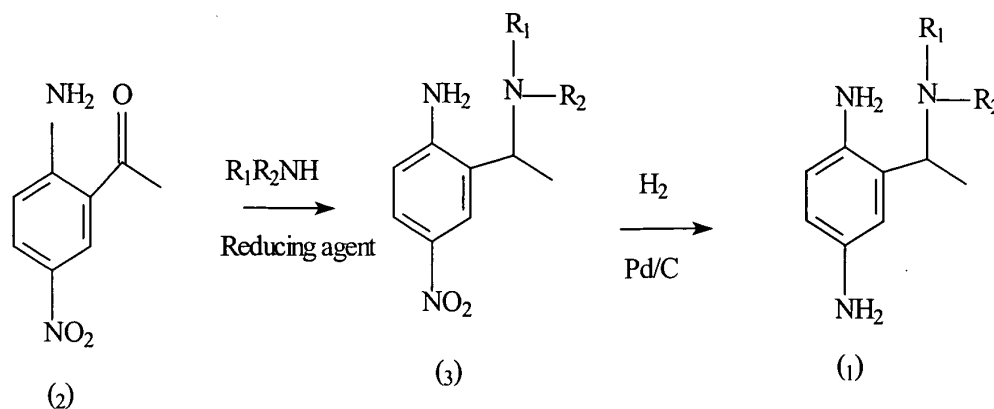


wherein R_1 and R_2 are each individually selected from a hydrogen atom, a C_1 to C_3 alkyl group, preferably methyl groups; phenyl or benzyl optionally substituted with an alkoxy group, preferably a methoxy group, or R_1 and R_2 together with the nitrogen atom to which they are bound form a piperazine, piperidine, imidazole, or morpholine ring.

Especially preferred compounds of formula (1) of this invention are the following compounds:

- 2-(1-phenylamino-ethyl)-benzene-1,4-diamine;
- 2-(1-piperidin-1-yl-ethyl)-benzene-1,4-diamine;
- 2-(1-benzylamino-ethyl)-benzene-1,4-diamine;
- 2-[1-(4-methoxy)-phenylamino-ethyl]-benzene-1,4-diamine;
- 2-(1-amino-ethyl)-benzene-1,4-diamine;
- 2-(1-dimethylamino-ethyl)-benzene-1,4-diamine;
- 2-(1-morpholin-4-yl-ethyl)-benzene-1,4-diamine;
- 2-(1-imadazolin-1-yl-ethyl)-benzene-1,4-diamine;
- 2-[1-(4-methoxy)-benzylamino-ethyl]-benzene-1,4-diamine
- 2-(1-methylaminol-ethyl)-benzene-1,4-diamine; and
- 2-(1-hydroxyethylamino-ethyl)-benzene-1,4-diamine.

The new benzene-1,4-diamine derivative compounds of formula (1) of this invention can be prepared according to the following reaction sequence wherein R_1 and R_2 are as defined hereinbefore.



5 In this synthesis procedure 2-amino-5-nitroacetophenone of formula (2) is subjected to reductive amination with the reagent R_1R_2NH using reducing agents such as $LiAlH_4$, DIBALH, $NaBH_4$, sodium triacetoxyborohydride, zinc borohydride, sodium cyanoborohydride, zinc acetate and polymethylhydrosiloxane (PMHS)/ $Ti(OiPr)_4$ to produce a compound of formula (3). Catalytic hydrogenation of the compound of formula 10 (3) with Pd/C under hydrogen produces a compound of formula (1).

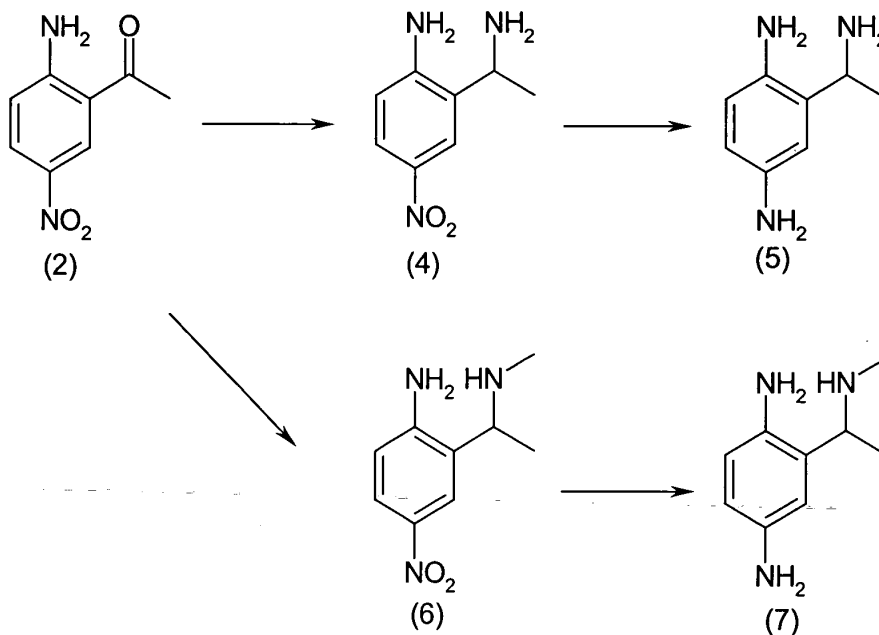
Synthesis Example 1

15 Synthesis of 2-(1-amino-ethyl)-benzene-1,4-diamine (5): To an autoclave at $-78^\circ C$ were added absolute ethanol (30 mL), liquid ammonia (30 mL), titanium (IV) isopropoxide (11.4 g, 40 mmol), and (2) (3.60 g, 20 mmol). The reaction mixture was stirred at $50^\circ C$ for 24 h and cooled to room temperature. After addition of sodium borohydride (1.14 g, 30 mmol), the mixture was 20 stirred for 24 h. Water was added to the reaction mixture and neutralized with 1N-NaOH aqueous solution, extracted with ethyl acetate (x3), dried with sodium sulfate and evaporated to afford (4) (900 mg, 24.8 % yield). The catalytic hydrogenation of (4) (900 mg, 5 mmol) with 10% Pd/C (0.1 g) in

ethyl acetate (50 mL) at 60 psi hydrogen at room temperature for 2.5 h produced (5) (740 mg, 98% yield).

Synthesis Example 2

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Synthesis of 2-(1-methylamino-ethyl)-benzene-1,4-diamine (7): To a solution of triethylamine (2.0 g, 20 mmol) in absolute ethanol (15 mL) were added methylamine hydrochloride (1.35 g, 20 mmol), titanium (IV) isopropoxide (5.7 g, 20 mmol), and (2) (1.80 g, 10 mmol). The reaction mixture was stirred at room temperature for 24 h and quenched with aqueous ammonium hydroxide (2N, 30 mL), filtered and washed dichloromethane. The organic layer was dried over sodium sulfate, filtered and evaporated to afford (6) (1.2 g, 61.5 % yield). Catalytic hydrogenation of (6) (1.2 g, 6.1 mmol) with 10 % Pd/C (0.24 g) in ethyl acetate (50 mL) at 60 psi hydrogen for 2.5 h afforded (7) (740 mg, 72.4 % yield).



Synthesis Examples 3 to 11

Employing the appropriate R_1R_2NH reagent, reducing agent and 2-amino-5-nitro-acetophenone in the synthesis procedure described, the following benzene-1,4-diamine derivative compounds of formula (1) of this invention can be prepared:

- 2-(1-phenylamino-ethyl)-benzene-1,4-diamine;
- 2-(1-piperidin-1-yl-ethyl)-benzene-1,4-diamine;
- 2-(1-benzylamino-ethyl)-benzene-1,4-diamine;
- 2-[1-(4-methoxy)-phenylamino-ethyl]-benzene-1,4-diamine;
- 2-(1-dimethylamino-ethyl)-benzene-1,4-diamine;
- 2-(1-morpholin-4-yl-ethyl)-benzene-1,4-diamine;
- 2-(1-imadazolin-1-yl-ethyl)-benzene-1,4-diamine;
- 2-[1-(4-methoxy)-benzylamino-ethyl]-benzene-1,4-diamine; and
- 2-(1-hydroxyethylamino-ethyl)-benzene-1,4-diamine.

As used herein, the term "hair dyeing composition" (also synonymously referred to herein as the hair dye composition, the hair coloring composition, or the hair dye lotion) refers to the composition containing oxidation dyes, including the novel compounds described herein, prior to admixture with the developer composition. The term "developer composition" (also referred to as the oxidizing agent composition or the peroxide composition) refers to compositions containing an oxidizing agent prior to admixture with the hair dyeing composition. The term "hair dye product" or "hair dye system" (also referred to as the hair dyeing system, hair dyeing product, or hair coloring system) interchangeably refer to the combination of the hair dyeing composition and the developer composition before admixture, and may further include a conditioner product and instructions, such product or system often being provided packaged as a kit. The term "hair dyeing product composition" refers to the composition formed by mixing the hair dyeing composition and the developer composition. "Carrier" (or vehicle or

base) refers to the combination of ingredients contained in a composition excluding the active agents (e.g., the oxidation hair dyes of the hair dyeing composition).

5 Hair coloring (i.e., hair dyeing) compositions of this invention can contain, in combination with oxidation dye couplers, a novel primary intermediate of this invention as the sole primary intermediate or can also contain other primary intermediates. Thus, one or more suitable primary intermediates may be used in combination with the novel primary
10 intermediates of this invention.

Suitable known primary intermediates include, for example,

p-phenylenediamine derivatives such as: benzene-1,4-diamine
15 (commonly known as p-phenylenediamine), 2-methyl-benzene-1,4-diamine, 2-chloro-benzene-1,4-diamine, N-phenyl-benzene-1,4-diamine, N-(2-ethoxyethyl)benzene-1,4-diamine, 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, (commonly known as N,N-bis(2-hydroxyethyl)-p-phenylenediamine) (2,5-diamino-phenyl)-methanol, 1-(2,5-diamino-phenyl)-
20 ethanol, 2-(2,5-diamino-phenyl)-ethanol, N-(4-aminophenyl)benzene-1,4-diamine, 2,6-dimethyl-benzene-1,4-diamine, 2-isopropyl-benzene-1,4-diamine, 1-[(4-aminophenyl)amino]-propan-2-ol, 2-propyl-benzene-1,4-diamine, 1,3-bis[(4-aminophenyl)(2-hydroxyethyl)amino]propan-2-ol, N⁴,N⁴,2-trimethylbenzene-1,4-diamine, 2-methoxy-benzene-1,4-diamine, 1-(2,5-diaminophenyl)ethane-1,2-diol, 2,3-dimethyl-benzene-1,4-diamine, N-(4-amino-3-hydroxy-phenyl)-acetamide, 2,6-diethylbenzene-1,4-diamine, 2,5-dimethylbenzene-1,4-diamine, 2-thien-2-ylbenzene-1,4-diamine, 2-thien-3-ylbenzene-1,4-diamine, 2-pyridin-3-ylbenzene-1,4-diamine, 1,1'-biphenyl-2,5-diamine, 2-(methoxymethyl)benzene-1,4-diamine, 2-(aminomethyl)benzene-
25 1,4-diamine, 2-(2,5-diaminophenoxy)ethanol, N-[2-(2,5-diaminophenoxy)ethyl]-acetamide, N,N-dimethylbenzene-1,4-diamine, N,N-diethylbenzene-1,4-diamine, N,N-dipropylbenzene-1,4-diamine, 2-[(4-

aminophenyl)(ethyl)amino]ethanol, 2-[(4-amino-3-methyl-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, N-(2-methoxyethyl)-benzene-1,4-diamine, 3-[(4-aminophenyl)amino]propan-1-ol, 3-[(4-aminophenyl)-amino]propane-1,2-diol, N-{4-[(4-aminophenyl)amino]butyl}benzene-1,4-diamine, and 2-[2-(2-{2-[(2,5-diaminophenyl)-oxy]ethoxy}ethoxy)ethoxy]benzene-1,4-diamine;

p-aminophenol derivatives such as: 4-amino-phenol (commonly known as p-aminophenol), 4-methylamino-phenol, 4-amino-3-methyl-phenol, 4-amino-2-hydroxymethyl-phenol, 4-amino-2-methyl-phenol, 4-amino-2-[(2-hydroxy-ethylamino)-methyl]-phenol, 4-amino-2-methoxymethyl-phenol, 5-amino-2-hydroxy-benzoic acid, 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol, 4-amino-2-(2-hydroxy-ethyl)-phenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-3-fluoro-phenol, 4-amino-2-(aminomethyl)-phenol, and 4-amino-2-fluoro-phenol;

o-aminophenol derivatives such as: 2-amino-phenol (commonly known as o-aminophenol), 2,4-diaminophenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, N-(4-amino-3-hydroxy-phenyl)-acetamide, and 2-amino-4-methyl-phenol; and

heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine (commonly known as 2,4,5,6-tetraaminopyridine), 1-methyl-1H-pyrazole-4,5-diamine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, N²,N²-dimethyl-pyridine-2,5-diamine, 2-[(3-amino-6-methoxypyridin-2-yl)amino]ethanol, 6-methoxy-N²-methyl-pyridine-2,3-diamine, 2,5,6-triaminopyrimidin-4(1H)-one, pyridine-2,5-diamine, 1-isopropyl-1H-pyrazole-4,5-diamine, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, 1-(benzyl)-1H-pyrazole-4,5-diamine, and 1-(4-chlorobenzyl)-1H-pyrazole-4,5-diamine.

The novel primary intermediates of formula (1) of this invention may be used with any suitable coupler(s) in hair coloring compositions or systems of this invention.

Suitable known couplers include, for example:

phenols, resorcinol and naphthol derivatives such as:

5 naphthalene-1,7-diol, benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methyl-naphthalen-1-ol, naphthalene-1,5-diol, naphthalene-2,7-diol, benzene-1,4-diol, 2-methyl-benzene-1,3-diol, 7-amino-4-hydroxy-naphthalene-2-sulfonic acid, 2-isopropyl-5-methylphenol, 1,2,3,4-tetrahydro-naphthalene-1,5-diol, 2-chloro-benzene-1,3-diol, 4-hydroxy-naphthalene-1-sulfonic acid, benzene-1,2,3-triol, naphthalene-2,3-diol, 5-dichloro-2-methylbenzene-1,3-diol, 4,6-dichlorobenzene-1,3-diol, and 2,3-dihydroxy-[1,4]naphthoquinone;

m-phenylenediamines such as: 2,4-diaminophenol, benzene-

15 1,3-diamine, 2-(2,4-diamino-phenoxy)-ethanol, 2-[(3-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, 2-methyl-benzene-1,3-diamine, 2-[[2-(2,4-diamino-phenoxy)-ethyl]-(2-hydroxy-ethyl)-amino]-ethanol, 4-{3-[(2,4-diaminophenyl)oxy]propoxy}benzene-1,3-diamine, 2-(2,4-diamino-phenyl)-ethanol, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 4-(2-amino-ethoxy)-

20 benzene-1,3-diamine, (2,4-diamino-phenoxy)-acetic acid, 2-[2,4-diamino-5-(2-hydroxy-ethoxy)-phenoxy]-ethanol, 4-ethoxy-6-methyl-benzene-1,3-diamine, 2-(2,4-diamino-5-methyl-phenoxy)-ethanol, 4,6-dimethoxy-benzene-1,3-diamine, 2-[3-(2-hydroxy-ethylamino)-2-methyl-phenylamino]-ethanol, 3-(2,4-diamino-phenoxy)-propan-1-ol, N-[3-(dimethylamino)phenyl]urea, 4-methoxy-

25 6-methylbenzene-1,3-diamine, 4-fluoro-6-methylbenzene-1,3-diamine, 2-[(3-[(2-hydroxyethyl)amino]-4,6-dimethoxyphenyl)-amino]ethanol, 3-(2,4-diaminophenoxy)-propane-1,2-diol, 2-[2-amino-4-(methylamino)-phenoxy]ethanol, 2-[(5-amino-2-ethoxy-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, 2-[(3-aminophenyl)amino]ethanol, N-(2-aminoethyl)benzene-1,3-

30 diamine, 4-[(2,4-diamino-phenyl)oxy]methoxy-benzene-1,3-diamine, and 2,4-dimethoxybenzene-1,3-diamine;

m-aminophenols such as: 3-amino-phenol, 2-(3-hydroxy-4-methyl-phenylamino)-acetamide, 2-(3-hydroxy-phenylamino)-acetamide, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, 5-amino-2,4-dichloro-phenol, 3-amino-2-methyl-phenol, 3-amino-2-chloro-6-methyl-phenol, 5-amino-2-(2-hydroxy-ethoxy)-phenol, 2-chloro-5-(2,2,2-trifluoro-ethylamino)-phenol, 5-amino-4-chloro-2-methyl-phenol, 3-cyclopentylamino-phenol, 5-[(2-hydroxyethyl)amino]-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 3-(dimethylamino)phenol, 3-(diethylamino)phenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichloro-phenol, 3-[(2-methoxyethyl)amino]phenol, 3-[(2-hydroxyethyl)amino]phenol, 5-amino-2-ethyl-phenol, 5-amino-2-methoxyphenol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(3-hydroxy-2-methylphenyl)-amino]propane-1,2-diol, and 3-[(2-hydroxyethyl)amino]-2-methylphenol; and

heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 6-methoxyquinolin-8-amine, 4-methylpyridine-2,6-diol, 2,3-dihydro-1,4-benzodioxin-5-ol, 1,3-benzodioxol-5-ol, 2-(1,3-benzodioxol-5-ylamino)ethanol, 3,4-dimethylpyridine-2,6-diol, 5-chloropyridine-2,3-diol, 2,6-dimethoxypyridine-3,5-diamine, 1,3-benzodioxol-5-amine, 2-[[3,5-diamino-6-(2-hydroxy-ethoxy)-pyridin-2-yl]oxy]-ethanol, 1H-indol-4-ol, 5-amino-2,6-dimethoxypyridin-3-ol, 1H-indole-5,6-diol, 1H-indol-7-ol, 1H-indol-5-ol, 1H-indol-6-ol, 6-bromo-1,3-benzodioxol-5-ol, 2-aminopyridin-3-ol, pyridine-2,6-diamine, 3-[(3,5-diaminopyridin-2-yl)oxy]propane-1,2-diol, 5-[(3,5-diaminopyridin-2-yl)oxy]pentane-1,3-diol, 1H-indole-2,3-dione, indoline-5,6-diol, 3,5-dimethoxypyridine-2,6-diamine, 6-methoxypyridine-2,3-diamine, and 3,4-dihydro-2H-1,4-benzoxazin-6-amine.

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Preferred primary intermediates include:

p-phenylenediamine derivatives such as: 2-methyl-benzene-1,4-diamine, benzene-1,4-diamine, 1-(2,5-diamino-phenyl)-ethanol, 2-(2,5-diamino-phenyl)-ethanol, N-(2-methoxyethyl)benzene-1,4-diamine, 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, and 1-(2,5-diaminophenyl)ethane-1,2-diol;

p-aminophenol derivatives such as 4-amino-phenol, 4-methylamino-phenol, 4-amino-3-methyl-phenol, 4-amino-2-methoxymethyl-phenol, and 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol;

o-aminophenol derivatives such as: 2-amino-phenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, N-(4-amino-3-hydroxy-phenyl)-acetamide, and 2-amino-4-methyl-phenol; and

heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine, 1-methyl-1H-pyrazole-4,5-diamine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, 1-(benzyl)-1H-pyrazole-4,5-diamine, and N²,N²-dimethyl-pyridine-2,5-diamine.

Preferred couplers include:

phenols, resorcinol and naphthol derivatives such as: naphthalene-1,7-diol, benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methyl-naphthalen-1-ol, naphthalene-1,5-diol, naphthalene-2,7-diol, benzene-1,4-diol, 2-methyl-benzene-1,3-diol, and 2-isopropyl-5-methylphenol;

m-phenylenediamines such as: benzene-1,3-diamine, 2-(2,4-diamino-phenoxy)-ethanol, 4-{3-[(2,4-diaminophenyl)oxy]propoxy}benzene-1,3-diamine, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 2-[2,4-diamino-5-

(2-hydroxy-ethoxy)-phenoxy]-ethanol, and 3-(2,4-diamino-phenoxy)-propan-1-ol;

5 m-aminophenols such as: 3-amino-phenol, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, and 3-amino-2-methyl-phenol; and

10 heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 1,3-benzodioxol-5-ol, 1,3-benzodioxol-5-amine, 1H-indol-4-ol, 1H-indole-5,6-diol, 1H-indol-7-ol, 1H-indol-5-ol, 1H-indol-6-ol, 1H-indole-2,3-dione, pyridine-2,6-diamine, and 2-aminopyridin-3-ol.

Most preferred primary intermediates include:

15 p-phenylenediamine derivatives such as: 2-methyl-benzene-1,4-diamine, benzene-1,4-diamine, 2-(2,5-diamino-phenyl)-ethanol, 1-(2,5-diamino-phenyl)-ethanol, and 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol;

20 p-aminophenol derivatives such as: 4-amino-phenol, 4-methylamino-phenol, 4-amino-3-methyl-phenol, and 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol;

25 o-aminophenols such as: 2-amino-phenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, and N-(4-amino-3-hydroxy-phenyl)-acetamide; and

30 heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, and 1-(benzyl)-1H-pyrazole-4,5-diamine.

Most preferred couplers include:

phenols, resorcinol and naphthol derivatives such as: benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methyl-naphthalen-1-ol, and 2-methyl-benzene-1,3-diol;

m-phenylenediamine such as: 2-(2,4-diamino-phenoxy)-ethanol, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 2-[2,4-diamino-5-(2-hydroxy-ethoxy)-phenoxy]-ethanol, and 3-(2,4-diamino-phenoxy)-propan-1-ol;

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m-aminophenols such as: 3-amino-phenol, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, and 3-amino-2-methyl-phenol; and

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heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 1H-indol-6-ol, and 2-aminopyridin-3-ol.

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Understandably, the coupler compounds and the primary intermediate compounds, including the novel compounds of the invention, in so far as they are bases, can be used as free bases or in the form of their physiologically compatible salts with organic or inorganic acids, such as hydrochloric, citric, acetic, tartaric, or sulfuric acids, or, in so far as they have aromatic OH groups, in the form of their salts with bases, such as alkali phenolates.

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The total amount of dye precursors (e.g., primary intermediate and coupler compounds, including the novel compounds of this invention) in the hair dyeing compositions of this invention is generally from about 0.002 to about 20, preferably from about 0.04 to about 10, and most preferably from about 0.1 to about 7.0 weight percent, based on the total weight of the hair dyeing composition. The primary intermediate and coupler compounds are

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generally used in molar equivalent amounts. However, it is possible to use the primary intermediate compounds in either excess or deficiency, i.e., a molar ratio of primary intermediate to coupler generally ranging from about 5:1 to about 1:5.

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The hair dyeing compositions of this invention will contain the primary intermediate of this invention in an effective dyeing amount, generally in an amount of from about 0.001 to about 10 weight percent by weight of the hair dye composition, preferably from about 0.01 to about 5.0 weight percent.

10 Other primary intermediates, when present, are typically present in an amount such that in aggregate the concentration of primary intermediates in the composition is from about 0.002 to about 10 weight percent, preferably from about 0.01 to about 5.0 weight percent. The coupler(s) are present in an effective dyeing concentration, generally an amount of from about 0.001 to
15 about 10.0 weight percent by weight of the hair dye composition, preferably from about 0.01 to about 5.0 weight percent. The remainder of the hair dye composition comprises a carrier or vehicle for the couplers and primary intermediates, and comprises various adjuvants as described below.

20 Any suitable carrier or vehicle, generally an aqueous or hydroalcoholic solution, can be employed, preferably an aqueous solution. The carrier or vehicle will generally comprise more than 80 weight percent of the hair dye composition, typically 90 to 99 weight percent, preferably 94 to 99 weight percent. The hair coloring compositions of this invention may contain
25 as adjuvants one or more cationic, anionic, amphoteric, or zwitterionic surface active agents, perfumes, antioxidants such as ascorbic acid, thioglycolic acid or sodium sulfite, chelating and sequestering agents such as EDTA, thickening agents, alkalizing or acidifying agents, solvents, diluents, inerts, dispersing agents, penetrating agents, defoamers, enzymes, and other dye
30 agents (e.g., synthetic direct and natural dyes). These adjuvants are cosmetic additive ingredients commonly used in compositions for coloring hair.

The hair dye compositions of the present invention are used by admixing them with a suitable oxidant, which reacts with the hair dye precursors to develop the hair dye. Any suitable oxidizing agent can be employed in the hair dye product compositions of this invention, particularly
5 hydrogen peroxide (H_2O_2) or precursors therefor. Also suitable are urea peroxide, the alkali metal salts of persulfate, perborate, and percarbonate, especially the sodium salt, and melamine peroxide. The oxidant is usually provided in an aqueous composition generally referred to as the developer composition, which normally is provided as a separate component of the
10 finished hair dye product and present in a separate container. The developer composition may also contain, to the extent compatible, various ingredients needed to form the developer composition, i.e., peroxide stabilizers, foam formers, etc., and may incorporate one or more of the adjuvants referred to above, e.g., surface active agents, thickeners, pH modifiers, etc. Upon mixing
15 the hair coloring composition and the developer composition to form a hair dye product composition, the adjuvants are provided in the hair dye product composition as it is applied to the hair to achieve desired product attributes, e.g., pH, viscosity, rheology, etc.

20 The form of the hair dye product compositions according to the invention can be, for example, a solution, especially an aqueous or aqueous-alcoholic solution. However, the form that is preferred is a thick liquid, cream, gel or an emulsion whose composition is a mixture of the dye ingredients with the conventional cosmetic additive ingredients suitable for the particular
25 preparation.

Suitable conventional cosmetic additive ingredients useful in the hair dye and developer compositions, and hence in the hair dye product compositions of this invention are described below, and may be used to
30 obtain desired characteristics of the hair dye, developer, and hair dye product compositions.

Solvents: In addition to water, solvents that can be used are lower alkanols (e.g., ethanol, propanol, isopropanol, benzyl alcohol); polyols (e.g., carbitols, propylene glycol, hexylene glycol, glycerin). See WO 98/27941 (section on diluents) incorporated by reference. See also US 6027538 incorporated by reference. Under suitable processing, higher alcohols, such as C8 to C18 fatty alcohols, especially cetyl alcohol, are suitable organic solvents, provided they are first liquified by melting, typically at low temperature (50 to 80 °C), before incorporation of other, usually lipophilic, materials.

10 The organic solvents are typically present in the hair dye compositions in an amount of from about 5 to about 30% by weight of the hair dye composition. Water is usually present in an amount of from about 5 to about 90% by weight of the hair dye composition, preferably from about 15 to about 75% by weight and most preferably from about 30 to about 65% by weight.

15 Surfactants: These materials are from the classes of anionic, cationic, amphoteric (including zwitterionic surfactants) or nonionic surfactant compounds. (Cationic surfactants, generally included as hair conditioning materials, are considered separately below.) Suitable surfactants, other than cationic surfactants, include fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkylsulfonates, alkylbenzensulfonates, alkyltrimethylammonium salts, alkylbetaines, ethoxylated fatty alcohols, ethoxylated fatty acids, ethoxylated alkylphenols, block polymers of ethylene and/orpropylene glycol, glycerol esters, phosphate esters, fatty acid alkanol amides and ethoxylated fatty acid esters, alkyl sulfates, ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, acyl isethionates, alkyl ethoxy carboxylates, fatty acid mono- and diethanolamides. Especially useful are sodium and ammonium alkyl sulfates, sodium and ammonium ether sulfates having 1 to 3 ethylene oxide groups, and nonionic surfactants sold as Tergitols, e.g., C11-C15 Pareth-9, and Neodols, e.g., C12-C15 Pareth-3. They are included for various reasons, e.g., to assist in thickening, for forming emulsions, to help in

wetting hair during application of the hair dye product composition, etc. Amphoteric surfactants include, for example, the asparagine derivatives as well betaines, sultaines, glycinate and propionates having an alkyl or alkylamido group of from about 10 to about 20 carbon atoms. Typical

5 amphoteric surfactants suitable for use in this invention include lauryl betaine, lauroamphoglycinate, lauroamphopropionate, lauryl sultaine, myristamidopropyl betaine, myristyl betaine, stearoamphopropylsulfonate, cocamidoethyl betaine, cocamidopropyl betaine, cocoamphoglycinate, cocoamphocarboxypropionate, cocoamphocarboxyglycinate, cocobetaine,

10 and cocoamphopropionate. Reference is made to WO 98/52523 published November 26, 1998 and WO 01/62221 published August 30, 2001, both incorporated herein by reference thereto.

The amount of surfactants in the hair dye compositions is

15 normally from about 0.1% to 30% by weight, preferably 1% to 15% by weight.

Thickeners: Suitable thickeners include such as higher fatty alcohols, starches, cellulose derivatives, petrolatum, paraffin oil, fatty acids and anionic and nonionic polymeric thickeners based on polyacrylic and polyurethane

20 polymers. Examples are hydroxyethyl cellulose, hydroxymethylcellulose and other cellulose derivatives, hydrophobically modified anionic polymers and nonionic polymers, particularly such polymers having both hydrophilic and hydrophobic moieties (i.e., amphiphilic polymers). Useful nonionic polymers include polyurethane derivatives such as PEG-150/stearyl alcohol/SDMI

25 copolymer. Suitable polyether urethanes are Aculyn® 44 and Aculyn® 46 polymers sold by Rohm & Haas. Other useful amphiphilic polymers are disclosed in US Pat. No. 6010541 incorporated by reference. See also WO 01/62221 mentioned above. Examples of anionic polymers that can be used as thickeners are acrylates copolymer, acrylates/ceteth-20 methacrylates

30 copolymer, acrylates/ceteth-20 itaconate copolymer, and acrylates/beheneth-25 acrylates copolymers. In the case of the associative type of thickeners, e.g., Aculyns 22, 44 and 46, the polymer may be included in one of either the

hair dye composition or the developer composition of the hair dye product and the surfactant material in the another. Thus, upon mixing of the hair dye and developer compositions, the requisite viscosity is obtained. The thickeners are provided in an amount to provide a suitably thick product as it is applied to the hair. Such products generally have a viscosity of from 1000 to 100000 cps, and often have a thixotropic rheology.

pH Modifying agents: Suitable materials that are used to adjust pH of the hair dye compositions include alkalizers such alkali metal and ammonium hydroxides and carbonates, especially sodium hydroxide and ammonium carbonate, ammonia, organic amines including methylethanolamine, aminomethylpropanol, mono-, di-, and triethanolamine, and acidulents such as inorganic and inorganic acids, for example phosphoric acid, acetic acid, ascorbic acid, citric acid or tartaric acid, hydrochloric acid, etc. See U.S. Patent 6027538 incorporated by reference.

Conditioners: Suitable materials include silicones and silicone derivatives; hydrocarbon oils; monomeric quaternary compounds, and quaternized polymers. Monomeric quaternary compounds are typically cationic compounds, but may also include betaines and other amphoteric and zwitterionic materials that provide a conditioning effect. Suitable monomeric quaternary compounds include behentrialkonium chloride, behentrimonium chloride, benzalkonium bromide or chloride, benzyl triethyl ammonium chloride, bis-hydroxyethyl tallowmonium chloride, C12-18 dialkyldimonium chloride, cetalkonium chloride, cetearrimonium bromide and chloride, cetrimonium bromide, chloride and methosulfate, cetylpyridonium chloride, cocamidopropyl ethyldimonium ethosulfate, cocamidopropyl ethosulfate, coco-ethyldimonium ethosulfate, cocotrimonium chloride and ethosulfate, dibehenyl dimonium chloride, dicetyldimonium chloride, dicocodimonium chloride, dilauryl dimonium chloride, disoydimonium chloride, ditallowdimonium chloride, hydrogenated tallow trimonium chloride, hydroxyethyl cetyl dimonium chloride, myristalkonium chloride, olealkonium

chloride, soyethomonium ethosulfate, soytrimonium chloride, stearalkonium chloride, and many other compounds. See WO 98/27941 incorporated by reference. Quaternized polymers are typically cationic polymers, but may also include amphoteric and zwitterionic polymers. Useful polymers are exemplified by polyquaternium-4, polyquaternium-6, polyquaternium-7, polyquaternium-8, polyquaternium-9, polyquaternium-10, polyquaternium-22, polyquaternium-32, polyquaternium-39, polyquaternium-44 and polyquaternium-47. Silicones suitable to condition hair are dimethicone, amodimethicone, dimethicone copolyol and dimethiconol. See also WO 99/34770 published July 15, 1999, incorporated by reference, for suitable silicones. Suitable hydrocarbon oils would include mineral oil.

Conditioners are usually present in the hair dye composition in an amount of from about 0.01 to about 5% by weight of the hair dye composition.

Direct Dyes: The hair dyeing compositions according to the invention can also contain compatible direct dyes including Disperse Black 9, HC Yellow 2, HC Yellow 4, HC Yellow 15, 4-nitro-o-phenylenediamine, 2-amino-6-chloro-4-nitrophenol, HC Red 3, Disperse Violet 1, HC Blue 2, Disperse Blue 3, and Disperse Blue 377. These direct dyes can be contained in the hair coloring compositions of the invention in an amount of from about 0.05 to 4.0 percent by weight.

Natural ingredients: For example, proteins and protein derivatives, and plant materials such as aloe, chamomile and henna extracts.

Other adjuvants include polysaccharides, alkylpolyglycosides, buffers, chelating and sequestrant agents, antioxidants, and peroxide stabilizing agents as mentioned in WO 01/62221, etc.

The adjuvants referred to above but not specifically identified that are suitable are listed in the International Cosmetics Ingredient Dictionary

and Handbook, (Eighth Edition) published by The Cosmetics, Toiletry, and
Fragrance Association, incorporated by reference. In particular reference is
made to Volume 2, Section 3 (Chemical Classes) and Section 4 (Functions)
are useful in identifying a specific adjuvant to achieve a particular purpose or
5 multipurpose.

The above-mentioned conventional cosmetic ingredients are
used in amounts suitable for their functional purposes. For example, the
surfactants used as wetting agents, associative agents, and emulsifiers are
10 generally present in concentrations of from about 0.1 to 30 percent by weight,
the thickeners are useful in an amount of from about 0.1 to 25 percent by
weight, and the hair care materials are typically used in concentrations of from
about 0.01 to 5.0 percent by weight.

15 The hair dyeing product composition as it is applied to the hair,
i.e., after mixing the hair dye composition according to the invention and the
developer, can be weakly acidic, neutral or alkaline according to their
composition. The hair dye compositions can have pH values of from about 6
to 11.5, preferably from about 6.8 to about 10, and especially from about 8 to
20 about 10. The pH of the developer composition is typically acidic, and
generally the pH is from about 2.5 to about 6.5, usually about 3 to 5. The pH
of the hair dye and developer compositions is adjusted using a pH modifier as
mentioned above.

25 In order to use the hair coloring composition for dyeing hair, the
above-described hair coloring compositions according to the invention are
mixed with an oxidizing agent immediately prior to use and a sufficient amount
of the mixture is applied to the hair, according to the hair abundance,
generally from about 60 to 200 grams. Some of the adjuvants listed above
30 (e.g., thickeners, conditioners, etc.) can be provided in the dye composition or
the developer, or both, depending on the nature of the ingredients, possible
interactions, etc., as is well known in the art.

Typically, hydrogen peroxide, or its addition compounds with urea, melamine, sodium borate or sodium carbonate, can be used in the form of a 3 to 12 percent, preferably 6 percent, aqueous solution as the oxidizing agent for developing the hair dye. Oxygen can also be used as the oxidizing agent. If a 6 percent hydrogen peroxide solution is used as oxidizing agent, the weight ratio of hair coloring composition and developer composition is 5:1 to 1:5, but preferably 1:1. In general, the hair dyeing composition comprising primary intermediate(s) and coupler(s), including at least one of the compounds of formula (1), is prepared and then, at the time of use, the oxidizing agents, such as H_2O_2 , contained in a developer composition is admixed therewith until an essentially homogenous composition is obtained, which is applied shortly after preparation to the hair to be dyed and permitted to remain in contact with the hair for a dyeing effective amount of time. The mixture of the oxidizing agent and the dye composition of the invention (i.e., the hair dye product composition) is allowed to act on the hair for about 2 to about 60 minutes, preferably about 15 to 45, especially about 30 minutes, at about 15 to 50°C, the hair is rinsed with water, and dried. If necessary, it is washed with a shampoo and rinsed, e.g., with water or a weakly acidic solution, such as a citric acid or tartaric acid solution. Subsequently the hair is dried. Optionally, a separate conditioning product may also be provided.

Together the hair dye composition of the present invention comprising the hair dye primary intermediate (1) and the developer composition comprising the oxidizing agent form a system for dyeing hair. This system may be provided as a kit comprising in a single package separate containers of the hair dye composition, the developer, the optional conditioner or other hair treatment product, and instructions for use.

Especially useful primary intermediates of formula (1) of this invention will provide hair coloring compositions having outstanding color fastness, especially light fastness, fastness to washing and fastness to rubbing.

Dyeing Example 1

The following composition shown in Table 1 can be used for dyeing Piedmont hair. 100 g of the dyeing composition is mixed with 100 g 20 volume hydrogen peroxide. The resulting mixture is applied to the hair and permitted to remain in contact with the hair for 30 minutes. The dyed hair is then shampooed, rinsed with water and dried. The ranges of ingredients set out in Table 1 are illustrative of useful concentrations of the recited materials in a hair dye product.

TABLE 1
Composition for Dyeing Hair

Ingredients	Range (wt %)	Weight (%)
Cocamidopropyl betaine	0-25	17.00
Polyquaternium-22	0-7	5.00
Monoethanolamine ¹	0-15	2.00
Oleic Acid	2-22	0.75
Citric Acid	0-3	0.10
28% Ammonium hydroxide ¹	0-15	5.00
Behentrimonium chloride	1-5	0.50
Sodium sulfite	0-1	0.10
EDTA	0-1	0.10
Erythorbic acid	0-1	0.40
Ethoxydiglycol	1-10	3.50
C11-15 Pareth-9 (Tergitol 15-S-9)	0.5-5	1.00
C12-15 Pareth-3 (Neodol 25-3)	0.25-5	0.50
Isopropanol	2-10	4.00
Propylene glycol	1-12	2.00
p-phenylenediamine	0-5	1 mmole
N,N-Bis(hydroxyethyl)-p-phenylene diamine	0-5	1 mmole
3-Methyl-p-aminophenol	0-5	1 mmole
p-Aminophenol	0-5	1 mmole
Primary Intermediate of this invention	0.5-5	4 mmoles
5-Amino-2-Methyl Phenol ²	0-5	3 mmoles
2,4-Diaminophenoxyethanol ²	0-5	3 mmoles
M-Phenylenediamine ²	0-5	1 mmole
Water	qs to 100.00	qs to 100.00

¹ In the aggregate, these ingredients are in the range of 2 to 15% by weight.

² At least one of these dye precursors is typically present.

Dyeing Example 2

5 A hair dye vehicle (or Base) was prepared containing the following ingredients: cocamidopropyl betaine 17 g; MEA 2.0 g; oleic acid 0.75 g; citric acid 0.1 g; 30% ammonium hydroxide 5.0 g; behentrimonium chloride 0.5 g; sodium sulfite 0.1 g; EDTA 0.1 g; erythorbic acid 0.4 g; ethoxydiglycol 3.5 g; C11-15 Pareth-9 1.0 g; C12-15 Pareth-3 0.5 g; isopropanol 4.0 g; propylene glycol 2.0 g, and water q.s. 100 g. Sufficient primary intermediate (as set forth

10 in Table 2) was added to an aliquot of Base to obtain a 0.025 M primary intermediate solution. Sufficient coupler (as also set forth in Table 2) was added to a second aliquot of Base to obtain a 0.025 M coupler solution. The developer composition was prepared containing the following ingredients: 50% hydrogen peroxide 12.0 g; Aculyn-22 1.0 g; Aculyn-33 12.0 g;

15 phosphoric acid to pH 3.5, and water q.s. 100g. Piedmont hair weighing from 700 to 900 mg was used in the dyeing tests. The hair dyeing composition was prepared by mixing 0.5 mL of the coupler solution with 0.5 mL of the primary intermediate solution, that mixture then being mixed with 1 mL of the developer composition. The hair dyeing composition was applied to hair

20 tresses mounted on a glass plate and then stored at 40°C for 30 minutes to allow the color to develop. The tresses were then washed, shampooed, and dried. Color of the hair was evaluated using the Minolta Spectrophotometer CM-3700d (Table 2).

TABLE 2

Color results of PPD derivatives (5) and (7) of Synthesis Examples 1 and 2

5

Primary Int.	Coupler	L*	a*	b*
5	2,4-diaminophenoxyethanol	39.1	-2.6	-7.8
7	2,4-Diaminophenoxyethanol	39.0	-2.4	-6.4
5	5-Amino-2-methylphenol	52.4	8.8	4.0
7	5-Amino-2-methylphenol	51.9	10.5	3.3
5	1-Naphthol	59.0	-0.2	5.0
7	1-Naphthol	54.3	0.6	1.0
5	Resorcinol	66.8	0.6	18.0
7	Resorcinol	64.2	1.4	16.2

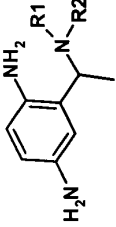

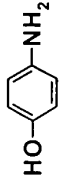
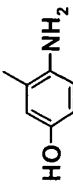
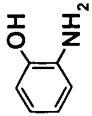
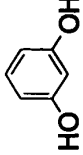
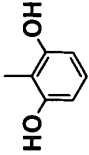
Exemplary combinations of hair coloring components employing a novel primary intermediate of formula (1) of this invention are shown in Tables 1 and 2, and in combinations C1 to C132 in Tables A through H. Reading down the columns in e.g., Table A, the Xes designate the dye compounds (including the novel primary intermediates of the instant invention) that form illustratively suitable combinations of dyes that can be formulated according to the present invention. For example, in Combination No. C1 in Column 4 of Table A, a primary intermediate of Formula 1 of this invention, wherein R¹ and R² are defined hereinbefore, can be combined with 2-amino-phenol.

Especially preferred as the primary intermediates in Table 1 and in combinations C1 to C132 of Tables A through H are:

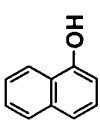
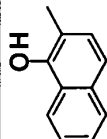
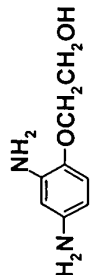
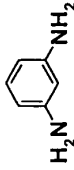
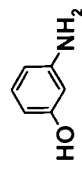
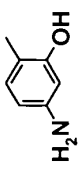
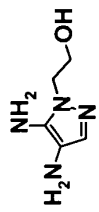
- 5 2-(1-phenylamino-ethyl)-benzene-1,4-diamine;
 2-(1-piperidin-1-yl-ethyl)-benzene-1,4-diamine;
 2-(1-benzylamino-ethyl)-benzene-1,4-diamine;
 2-[1-(4-methoxy)-phenylamino-ethyl]-benzene-1,4-diamine;
 2-(1-amino-ethyl)-benzene-1,4-diamine;
 2-(1-dimethylamino-ethyl)-benzene-1,4-diamine;
10 2-(1-morpholin-4-yl-ethyl)-benzene-1,4-diamine;
 2-(1-imadazolin-1-yl-ethyl)-benzene-1,4-diamine;
 2-[1-(4-methoxy)-benzylamino-ethyl]-benzene-1,4-diamine
 2-(1-methylaminol-ethyl)-benzene-1,4-diamine; and
 2-(1-hydroxyethylamino-ethyl)-benzene-1,4-diamine.
- 15

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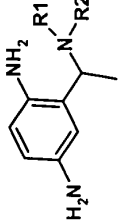

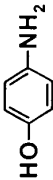
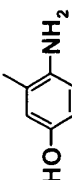
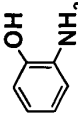
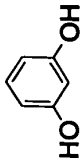
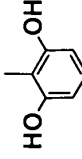
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Table A. Dye Combinations													
Structure	IUPAC Name	Name	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
			x	x	x	x	x	x	x	x	x	x	x
	2-[(4-Amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol	N,N-Bis(2-hydroxyethyl)-p-phenylene-diamine											
	4-Amino-phenol	p-Aminophenol											
	4-Amino-3-methyl-phenol	3-Methyl-p-aminophenol											
	2-Amino-phenol	o-Aminophenol	x									x	
	Benzene-1,3-diol	Resorcinol		x								x	x
	2-Methyl-benzene-1,3-diol	2-Methyl-resorcinol			x								x

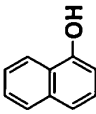
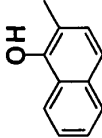
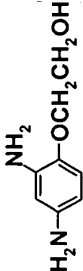
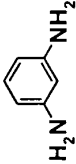
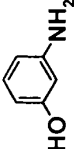
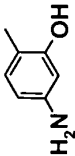
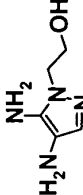
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Table A (continued). Dye Combinations													
Structure	IUPAC Name	Name	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
	Naphthalen-1-ol	1-Naphthol				X							
	2-Methyl-naphthalen-1-ol	2-Methyl-1-naphthol					X						
	2-(2,4-Diamino-phenoxy)-ethanol	2,4-Diamino-phenoxyethanol						X					
	Benzene-1,3-diamine	m-Phenylenediamine							X				
	3-Amino-phenol	m-Aminophenol								X			
	5-Amino-2-methyl-phenol	2-Hydroxy-4-aminotoluene									X		
	2-(4,5-Diamino-pyrazol-1-yl)-ethanol	1-Hydroxyethyl-4,5-diamino-pyrazole											

208110-1225001

Table B. Dye Combinations														
Structure	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25
	X	X	X	X	X	X	X	X	X	X	X	X	X	X
														
														
														
							X							
	X	X	X	X	X	X		X						
							X	X	X	X	X	X	X	X

208770-12825001

Table B (continued). Dye Combinations																		
Structure	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29
	X								X									X
		X								X								
			X								X							
				X								X						
					X								X					
						X								X				
																		

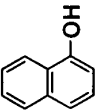
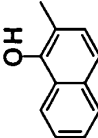
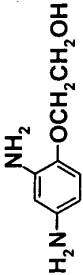
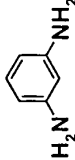
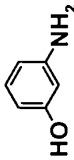
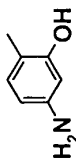
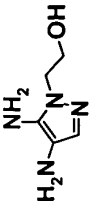
208110-1225001

Table C. Dye Combinations

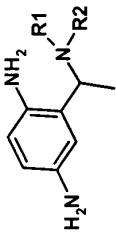

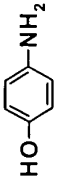
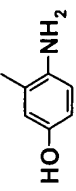
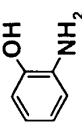
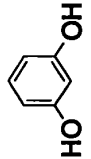
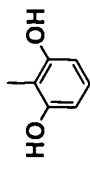
Structure	C30	C31	C32	C33	C34	C35	C36	C37	C38	C39	C40	C41	C42	C43	C44	C45	C46	C47
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	X	X	X	X	X											X	X	X
						X										X		
							X									X	X	X
								X									X	

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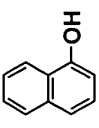
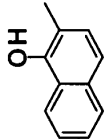
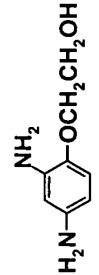
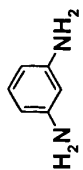
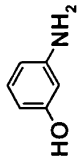
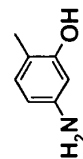
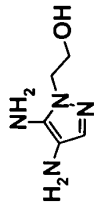
Table C (continued). Dye Combinations

Structure	C30	C31	C32	C33	C34	C35	C36	C37	C38	C39	C40	C41	C42	C43	C44	C45	C46	C47
									x									x
	x									x								
		x									x							
			x									x		x	x			
				x		x	x	x	x	x	x	x	x	x	x			
					x													
						x	x	x	x	x	x	x	x	x	x			

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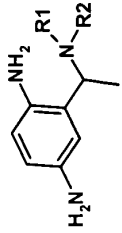

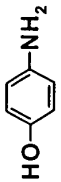
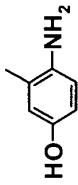
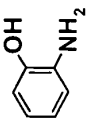
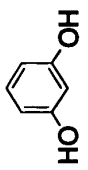
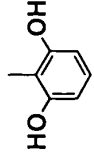
Table D. Dye Combinations																		
Structure	C48	C49	C50	C51	C52	C53	C54	C55	C56	C57	C58	C59	C60	C61	C62	C63	C64	C65
	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
	x	x	x	x	x													
						x	x	x	x	x	x	x	x	x				
															x	x	x	x
						x									x			
	x	x	x	x	x		x									x		
								x									x	

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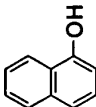
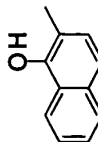
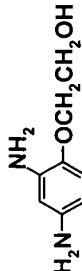
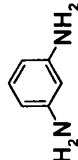
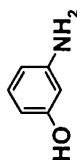
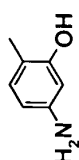
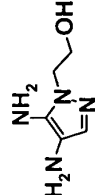
Table D (continued). Dye Combinations																		
Structure	C48	C49	C50	C51	C52	C53	C54	C55	C56	C57	C58	C59	C60	C61	C62	C63	C64	C65
									X									X
	X									X								
		X									X							
			X									X						
				X									X					
					X									X				
																		

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Table E. Dye Combinations

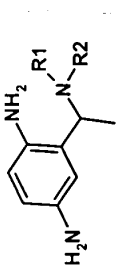

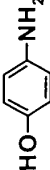
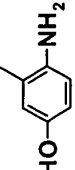
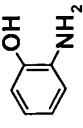
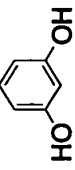
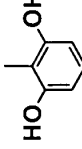
Structure	C66	C67	C68	C69	C70	C71	C72	C73	C74	C75	C76	C77	C78	C79	C80	C81	C82	C83
	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
																		
																		
	x	x	x	x	x													
						x									x			
							x								x	x	x	x
								x								x		

20210722E0001

Table E (continued). Dye Combinations																		
Structure	C66	C67	C68	C69	C70	C71	C72	C73	C74	C75	C76	C77	C78	C79	C80	C81	C82	C83
									X								X	
	X									X								X
		X									X							
			X									X						
				X									X					
					X									X				
						X		X	X	X	X	X	X	X	X	X	X	X

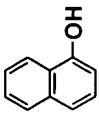
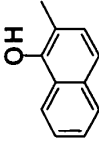
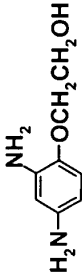
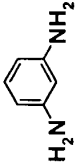
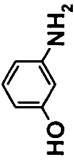
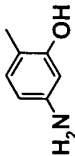
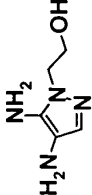
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Table F. Dye Combinations

Structure	C84	C85	C86	C87	C88	C89	C90	C91	C92	C93	C94	C95	C96	C97	C98	C99	C100	C101
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
																		
					X	X	X	X	X	X	X	X	X					
															X	X	X	X
					X									X				
	X	X	X	X		X									X			
							X									X		

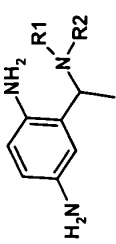

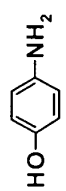
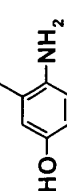
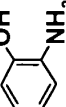
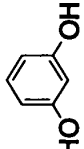
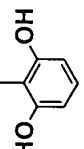
208TFO" TEE250DT

Table F (continued). Dye Combinations

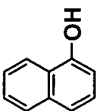
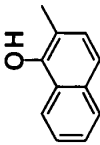
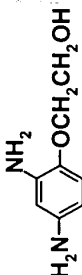
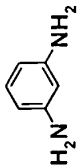
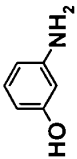
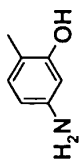
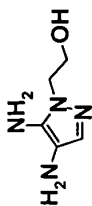
Structure	C84	C85	C86	C87	C88	C89	C90	C91	C92	C93	C94	C95	C96	C97	C98	C99	C100	C101
								x									x	
									x									x
	x									x								
		x									x							
			x									x						
				x									x					
	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x

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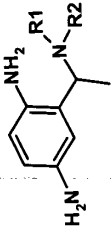

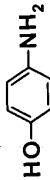
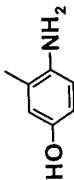
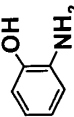
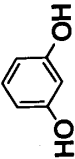
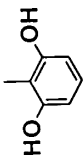
Table G. Dye Combinations

Structure	C102	C103	C104	C105	C106	C107	C108	C109	C110	C111	C112	C113	C114	C115	C116	C117	C118	C119
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
					X	X	X	X	X	X	X	X	X	X	X	X	X	X
					X	X	X	X	X	X	X	X	X					
	X	X	X	X										X	X	X	X	X
					X									X				
						X									X			
							X									X		

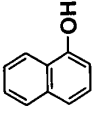
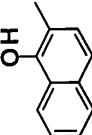
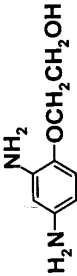
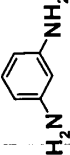
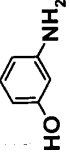
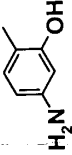
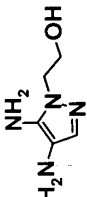
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Table G (continued). Dye Combinations																		
Structure	C102	C103	C104	C105	C106	C107	C108	C109	C110	C111	C112	C113	C114	C115	C116	C117	C118	C119
								X									X	
									X									X
	X									X								
		X									X							
			X									X						
			X	X									X					
	X	X	X	X														

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Table H. Dye Combinations													
Structure	C120	C121	C122	C123	C124	C125	C126	C127	C128	C129	C130	C131	C132
	X	X	X	X	X	X	X	X	X	X	X	X	X
	X	X	X	X	X	X	X	X	X	X	X	X	X
													
	X	X	X	X									
					X								
						X							
							X						

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Table H (continued). Dye Combinations													
Structure	C120	C121	C122	C123	C124	C125	C126	C127	C128	C129	C130	C131	C132
								X					
									X				
	X									X			
		X									X		
			X									X	
				X									X
													X

With the foregoing description of the invention, those skilled in the art will appreciate that modifications may be made to the invention without departing from the spirit thereof. Therefore, it is not intended that the scope of

5 the invention be limited to the specific embodiments illustrated and described.

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